Available online at www.sciencedirect.com

ScienceDirect

Procedia Environmental Sciences 4 (2011) 76–86

Procedia Environmental Sciences

Urban Environmental Pollution 2010

Contribution of point sources to trace metal levels in urban areas surrounded by industrial activities in the Cantabria Region (Northern Spain)

S. Ruiz, A. Arruti, I. Fernández-Olmo*, J.A. Irabien

Departamento de Ingeniería Química y Química Inorgánica. ETSIIyT Universidad de Cantabria. Avda. de los Castros s/n. 39005 Santander. Spain

Received date September 30, 2010; revised date January 30, 2011; accepted date January 30, 2011

Abstract

The present work deals with the characterization of selected heavy metals (Ti, V, Cr, Mn, Cu, Mo, Pb, Ni, Cd and As) in PM10 collected in 2008 in three urban areas of Cantabria (Northern Spain) which are influenced by industrial activities. Ternary plots were used to identify the main tracers at the studied sites. Pollutant roses of these tracers were used as tools which give information about the location of the most important emission sources due to the characteristic wind patterns in Cantabria. Pollutant roses showed a significant contribution of the local industry to trace metal levels at the selected urban sites.

Keywords: urban air quality; trace metals; PM10; pollutant roses; industrial impact.

1. Introduction

The study of the levels and composition of particulate matter (PM) is directly linked to the proven adverse effects on human health [1]. In this context, it is important to note that some trace element emissions are due to natural processes but large amounts of these pollutants result from anthropogenic activities such as combustion of fossil hydrocarbons, metallurgical industries and traffic [2]. Some of these trace elements may be used as tracers of some emission sources [3].

There are three main groups of source apportionment techniques which aim to link the impacts of emissions of atmospheric pollutants from different sources with the levels of such pollutants at receptor sites [4]: methods based on the evaluation of monitoring data, for example by correlating meteorological variables with levels of air pollutants [5]; methods based on emission data, by means of inventories or direct measurements of pollutants, in order to model the dispersion, transformation, transport and deposition of such contaminants [6]; and, methods based on the statistical evaluation of the pollutants measured at receptor sites (e.g. Principal Component Analysis, Positive Matrix Factorization or Chemical Mass Balance) [7]. Pollutant roses are included in the first kind of

* Corresponding author. Tel.: +34-942201470; fax: +34-942201591.
E-mail address: fernandi@unican.es

doi:10.1016/j.proenv.2011.03.010

methods and they are polar diagrams that show how air pollution depends on wind direction. If an ambient air quality monitoring station is markedly influenced by a source of the pollutant measured, the pollutant rose shows a peak towards the local source [8]. Rose analysis is a commonly used tool in source apportionment on regional scales [9-10] and for identifying local point sources [11-13].

The analysis of pollution levels as a function of the meteorological conditions which may influence the fate of PM is useful for a better characterisation of heavy metal behaviours [14] but it always creates some problems due to the variability of most meteorological parameters over a large period of sampling, such as that required for metal analysis, typically 24 hours [15]. In order to avoid the problems derived from the low time-resolution of metal data and possible misinterpretation of the final results, two strategies have been found in the literature: first, the development of real-time samplers has resulted in the ability to obtain high time-resolved particle composition data like Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) [16]. Second, there are some studies about techniques based on computational schemes to derive pollution roses from 24 h metal concentration data and wind direction data recorded hourly [8,17-18]. A similar approach was performed by Gladtke et al. [5] using calculated PM10 and metal roses in an industrial area from 24 h surplus concentration data and 0.5 h wind direction data; surplus concentration data were first obtained by subtracting the background levels of these pollutants measured in sites not directly affected by point sources.

The objective of the present work is to carry out a qualitative assessment of the impact of some local industrial sources on trace metal levels in PM10 in the main urban areas of Cantabria Region (Northern Spain). As described below, ternary plots were used to identify the main tracers at the sampling areas. Next, pollutant roses of these tracers from 24 and 48 h metal concentration data and 1 h wind direction data were calculated to help in the interpretation of the qualitative impact of the most important emission sources on trace metal levels at the selected urban sites.

2. Methodology

2.1. Study area

Cantabria is located in Northern Spain. It is surrounded by Cantabrian Sea and Cantabrian mountains (Fig. 1). It is characterized by a wet Atlantic weather with an annual average temperature of 14ºC and an annual average precipitation of 1,246 mm (with a mean relative humidity of 75%).

Figure 1. Location of the study area

Three urban areas were selected in order to study the influence of the industrial activity in the air quality of the region (Fig. 2):

- *Santander* (182,700 inhabitants, 2008) is the most important city of the region. The city is in close vicinity to an industrial area, which is mostly related to iron, steel and ferro-manganese alloys manufacturing plants. One monitoring site was placed in this area: SANT is an urban background station, located on the rooftop of the building "E.T.S de Ingenieros Industriales y de Telecomunicaciones" (SANT; 43º28´26´´N, 3º47´47´´W, 23 m.a.s.l.), which is close to the Sardinero beaches zone. Additionally, data from an industrial station located close to a ferro-manganese alloys production plant, 7 Km SSW from SANT site (ALM; 43º24´55´´N, 3º50´5´´W) were also used. ALM data were kindly provided by the Regional Environmental Ministry of Cantabria Government according to the Directive 2003/4/EC on public access to environmental information.

- *Torrelavega* (55,910 inhabitants, 2008) is the second largest town at the region which is located in a valley 23 Km away from Santander. The town has a prominent industrial sector dominated by pulp and chemical plants with an intense use of fossil fuels. The monitoring station, TORR, is placed in Barreda (TORR; 43º22´3´´N, 4º2´34´´W, 18 m.a.s.l) and it is an urban background station with some traffic and industrial influence.
- *Castro Urdiales* (31,670 inhabitants, 2008) is a coastal town in the east of Cantabria located 10 Km WNW from a petrochemical plant and 15-20 Km WNW from a fuel-oil power station and some metallurgical plants. An urban background monitoring station was also placed (CAST; 43º22´56´´N, 3º13´14´´W, 20 m.a.s.l).

Fig. 2 shows the location of the monitoring sites together with the metals emitting point sources situated in the vicinity of these sites. The emission sources of metals were obtained from the emission inventory provided by the e-PRTR (the European Pollutant Release and Transfer Register), an easily accessible key environmental data from industrial facilities in European Union Member States.

2.2. PM sampling and analysis

PM10 was sampled in 2008 at the three selected urban background sampling sites. Periods of 24 h sampling were carried out at SANT site; 48 h monitoring samples were collected by the Regional Environmental Ministry of Cantabria Government at TORR and CAST stations. PM10 sampling at SANT was performed by means of an EN-UNE 12341 equivalent high volume sampler (MCV, operation conditions: 30 m^3/h) using glass fiber filters (150 mm of diameter), while samples from TORR and CAST sites were obtained from low volume samplers (2.3 m^3/h) using quartz micro-fiber filters (47 mm diameter, Sartorious). Then, the content of ten heavy metals (Ti, V, Cr, Mn, Cu, Mo, Pb, Ni, Cd and As) is determined in PM10 samples by UNE-EN 14902:2006 methodology (Standard method for the measurements of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter). Each filter is digested using a mix of HNO_3 and H_2O_2 in a microwave digestion system (ETHOS) with Teflon beakers at a given temperature program. After cooling, the solution is diluted to a volume of 50 ml and this solution is analyzed by ICP-MS (Agilent 7500C). The blank contribution from filters and reagents has been evaluated and subtracted from the results. Further details about the analytical methodology, accuracy and precision and detection limits can be found in Arruti et al. [19]. A minimum of 14% of the annual sampling period was selected for chemical analysis in order to fulfill the requirements of the air quality directive for indicative measurements (Directive 2004/107/EC). The number of samples where the metal levels were determined is shown in table 1.

This study is completed with PM10 and trace metal concentration data supplied by the Regional Environmental Ministry of Cantabria Government at ALM site in 2009.

The meteorological parameters including wind direction and speed were supplied by the Air Quality Monitoring Network of the Regional Environmental Ministry of Cantabria Government.

2.3 Ternary plots

The ternary diagrams may be used to compare the concentrations of metals measured at three sampling sites; these diagrams are commonly used in the Earth Sciences to represent the relative contents of different components [20]; in the present work, the ternary diagram represents the spatial variation of the annual mean trace metal concentration at the three urban sites (SANT, TORR and CAST).

The trace metals levels values (ng/m^3) at SANT, TORR and CAST were previously transformed to µg/g, in order to eliminate the effect of the PM10 mass. Each point in the ternary diagram represents the percentage of the studied trace metal distributed among the three urban sites. The sum of the contributions for each studied metal must be 100%.

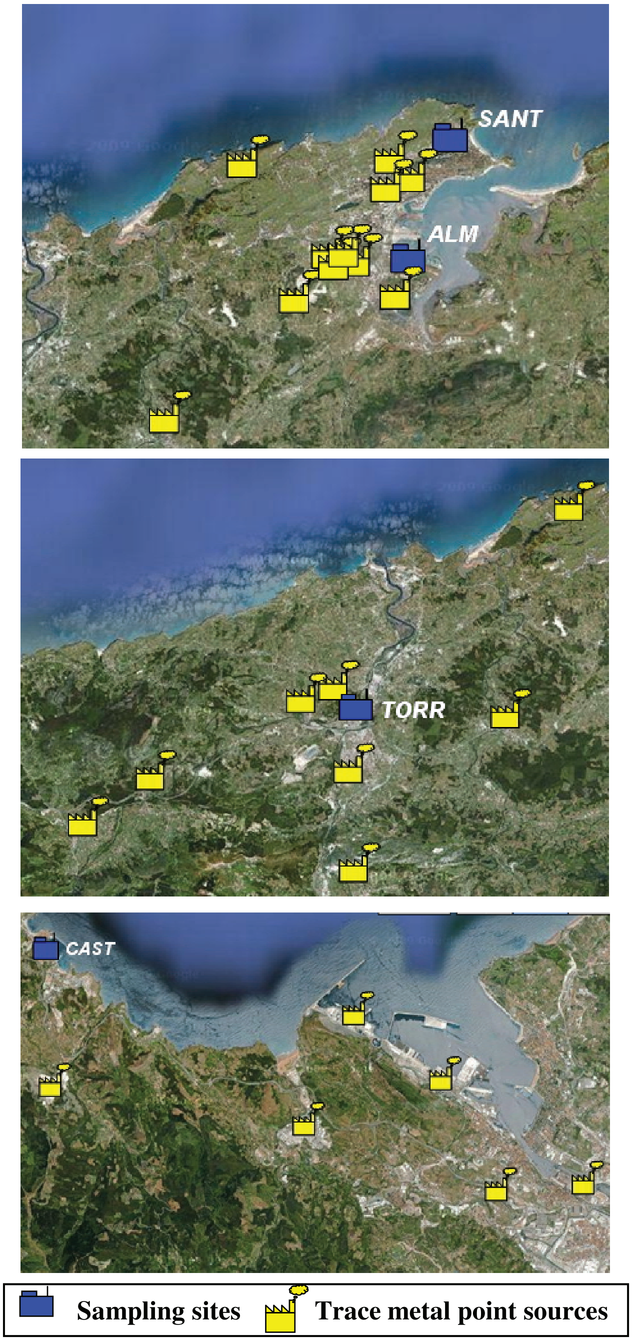


Figure 2. Location of the studied sampling sites and metals emitting point sources: a) Santander; b) Torrelavega and c) Castro Urdiales

Since the emission sources are not the same at the three urban sites, an elevated concentration of a typical source tracer explains a higher impact of this emission source; therefore, in the ternary diagram the typical source tracer is shown closer to the corner representing the studied urban site [20]. The advantage of the ternary diagrams is that the interpretation is easier than other plots such as those produced by PCA [21].

2.4. Computation of pollutant roses

When the pollutant data are averages over 24 h, as is the case of heavy metals, the construction of a pollutant rose requires a mathematical methodology to obtain high quality plots. The trace metal roses calculated in this work are based on the methodology developed by Cosemans and Kretzschmar [18] where the measurements are divided into 36 partitions, each partition corresponding to a 10º wind direction sector according to:

$$c_i = \sum_{j=1,n} p_j \cdot f_{i,j} \cdot \alpha_j \Big/ \sum_{j=1,n} f_{i,j} \cdot \alpha_j \qquad (1)$$

where:

- j: day index for the period under investigation.
- n: the number of days in the period for which the rose is constructed.
- i: the wind sector index for the rose. Range 1-36 for sectors of 10º.
- c_i: the resulting average concentration for wind sector *i* in all the studied period.
- p_j: the measured concentration on day *j*.
- $f_{i,j:}$ the number of hours that the wind came from sector *i* on day *j*.
- α_j: some weight function based on the persistency of the wind vector during day *j*.

In this case, α_j is set to the inverse of the number of wind direction bins on day *j* with non-zero frequency, n_j.

$$\alpha_j = 1/n_j \qquad (2)$$

This means that if the wind pattern of a given day is well distributed, n_j will be high (the maximum value would be 24), and therefore α_j will be small; then, the wind dispersion of this day will lead to a small weight of the pollutant concentration. On the other hand, when wind blows only from one or two sectors for a given day, α_j will be higher; so, the weight of the pollutant concentration will be higher.

The computed pollutant rose is a vector with dimension equal to the number of sectors used, in this case 36.

3. Results and discussion

3.1. Levels of trace metals

The concentration of the studied trace metals in PM10 at SANT, ALM, TORR and CAST sites is shown in Table 1. The mean, standard deviation, maximum and minimum concentrations are given in the table. The highest average annual PM10 levels were registered at SANT and TORR sites (30 µg/m^3); all the PM10 values at the Cantabria Region are below the annual limit, 40 µg/m^3 (Directive 1999/30/EC). Moreover, the PM10 levels in the Cantabria Region are in the range of the levels reported in other European cities [22].

The trace metals levels in PM10 affected by the EC directives, Pb, As, Ni and Cd, were lower than the EC proposed annual limit or target values; 6, 20 and 5 ng/m^3 for As, Ni and Cd, respectively (Directive 2004/107/EC) and 500 ng/m^3 for Pb (Directive 1999/30/EC). The urban annual values for V and Mn did not exceed the WHO air quality guideline values, 1000 ng/m^3 and 150 ng/m^3, respectively; however, the WHO air quality guideline value for Mn was exceed at ALM industrial site. A comparison between trace metal levels in PM10 at different European urban sites is carried out in table 2. With regard to other Spanish urban sites, table 2 reveals the high levels of Mn at SANT site (49.1 ng/m^3) and Cr at TORR site (25.8 ng/m^3). The Mn and Cr concentration values are higher than those reported at other Spanish urban sites, except in Llodio case; Llodio town is highly influenced by emissions from industrial activities [23]. The concentration value of other trace metals, such as Pb or Cd, at the Cantabria Region were in the Spanish concentration range; even, the levels of some metals, such as Ti and Mo, were below the Spanish range, as shown in table 2.

Table 1. Mean (M), standard deviation (S.D.), minimum (Min) and maximum (Max) concentrations of PM10 ($\mu g/m^3$) and trace metal in PM10 (ng/m^3) measured in the monitoring sites. N is the number of samples.

		PM10	*Pb*	*As*	*Ni*	*Cd*	*Ti*	*V*	*Cr*	*Mn*	*Cu*	*Mo*
SANT*	M	29	6.2	0.5	0.9	0.3	2.4	1.2	2.1	49.1	3.7	0.5
	S.D.	12.9	6.71	0.47	0.81	0.47	2.44	0.85	0.51	60.8	3.93	0.48
	Min	11.1	<0.7	<0.5	<0.4	<0.1	<1.9	<0.03	<3.8	<1.8	<0.1	<0.05
	Max	64.5	30.9	2.4	4.2	2.9	10.7	4.1	4.1	242.0	16.8	1.8
	N	117	50	50	50	50	50	50	50	50	50	50
ALM*(1)	M	24	28.7	0.6	5.0	0.8		1.8	3.1	1071.7	10.0	1.2
	S.D.	11.4	30.1	0.36	8.2	0.85		1.5	2.9	1436.5	6.6	0.66
	Min	8	<0.009	<0.1	<0.8	<0.1		<0.9	<0.9	<0.9	<0.9	<0.9
	Max	86	160.0	1.6	54.8	5.2		7.2	20.6	8859.6	33.5	4.2
	N	278	108	108	108	108		108	108	108	108	108
TORR**	M	30.6	12.5	0.2	2.8	0.2	5.4	2.0	25.8	23.7	18.9	1.2
	S.D.	15.8	10.7	0.15	2.5	0.19	8.1	1.4	58.8	18.4	10.5	0.75
	Min	8	2.0	<0.03	<1.0	<0.01	<1.2	0.2	<2.3	<1.1	<1.1	<0.2
	Max	106	44.1	0.7	10.4	0.7	41.8	6.0	285.6	76.5	44.9	3.9
	N	362	29	29	29	29	29	29	29	29	29	29
CAST**	M	21.5	7.7	0.2	3.0	0.09	5.2	3.1	<2.3	9.3	3.5	0.5
	S.D.	9.4	8.5	0.19	2.7	0.15	4.2	3.7	2.1	8.0	4.1	0.7
	Min	4	0.6	0.06	1.0	0.01	1.3	0.1	<2.3	3.5	1.2	<0.2
	Max	59	39.9	0.7	12.8	0.6	16.6	19.1	9.3	31.7	15.1	2.7
	N	351	28	28	28	28	28	28	28	28	28	28

* These statistical values are calculated from samples collected for 24 hours

** These statistical values are calculated from samples collected for 48 hours

(1) ALM data were supplied by the Regional Environmental Ministry of Cantabria Government.

3.2. Identification of main tracers

A ternary diagram is used in this work to identify the main tracers from each sampling site (Fig. 3). This figure displays how this plot could show the dominance of the potential main tracer from each studied site.

Thus, Mn is the main tracer found in Santander; it can be linked to steel and ferromanganese alloys manufacturing plants [31-32]. The diagram also shows that Cu and Cr are the main tracers in Torrelavega, this observation agrees with the presence of a heavy-traffic motorway and several chemical plants with an intensive use of fossil fuels in this area. Lastly, Ni and V are oriented through Castro Urdiales corner; additionally, an important contribution of these metals on Torrelavega site is observed in the diagram; this can be due to the use of fossil fuels in some industries located in the Torrelavega area. However, taking into account that a petrochemical plant is located 10 Km SE from Castro Urdiales and that Ni and V have been identified in the literature as main tracers of petrochemical industry [33], these metals have been selected as main tracers of Castro Urdiales urban area.

3.3. Pollution roses of selected tracers

Finally, pollution roses were plotted for each main tracer found at the three selected sites. Figure 4 shows the roses of Mn at Santander bay, calculated at SANT and ALM sites using equation (1). They show the highest peaks pointing into the direction of industrial areas which are characterized by steel and ferromanganese factories. However, elevated Mn concentrations from sectors oriented to NE are also observed, probably due to the characteristic NE see breezes found in the summer season at Santander bay. This characteristic wind pattern is shown in Figure 5, where the wind roses of the two days with the highest Mn concentration are plotted. During these days, light winds blew predominantly from the SW in the morning but, at noon, they reversed direction to become NE-ENE onshore moderate sea breezes which return the industrial pollution plume inland, thus raising the Mn concentration at the sampling sites [34].

Table 2: Comparison of trace metal mean levels in urban PM10 (ng/m^3) with previous studies.

		Pb	As	Ni	Cd	Ti	V	Cr	Mn	Cu	Mo
Spain	Santander[a]	6.2	0.5	0.9	0.3	2.4	1.2	2.1	49.1	3.7	0.5
	Castro[a]	7.7	0.2	3.0	0.1	5.2	3.1	<2.3	9.3	3.5	0.5
	Torrelavega[a]	12.5	0.2	2.8	0.2	5.4	2.0	25.8	23.7	18.9	1.2
	Llodio[b]	103	1.8	33	1.2	25	8	25	87	33	16
	Huelva[b]	37	5.4	4	0.8	60	7	2	11	70	5
	Tarragona[b]	26	0.8	4	0.3	23	8	3	9	33	2
	Zaragoza[c]	18.7		0.8			6.6	7.7	24.7		
	Spanish urban range[d]	7-57	0.3-1.6	2-7	0.1-0.7	18-83	2-15	2-8	4-23	7-88	2-5
Switzerland	Zurich[e]	20	0.4	1.8			1.0		7.3	17	1.3
Greece	Athens[f]	34.3	3.7	9.0	2.4		9.5	11.0	13.9	40.0	
France	Dunkerke[g]	34	2.5	9.4	1.3	17.0	15.9	4.9	99	15.6	2.1
Italy	Palermo[h]	20	1.8	3.7			22	3.9	9.3	24	1.8
	Trieste[i]	17.4	0.7	6.8	0.4		13.3	1.9	10.9		

[a]Present study; [b] [24]; [c] [25]; [d] [23]; [e] [26]; [f] [27]; [g] [28]; [h] [29]; [i] [30].

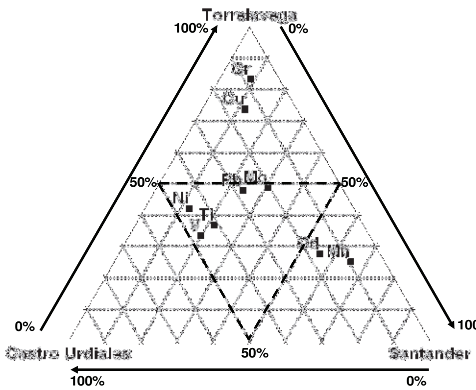


Figure 3. Ternary plots for the studied heavy metals at the three sampling sites

At Torrelavega, roses show different sources for each tracer (Fig. 6). On one hand, Cu presents a homogeneous distribution that could be caused by the heavy traffic of the motorway and adjacent roads due to this trace element is associated with diesel engines and wearing of break vehicles [25]. Cr peaks are oriented towards the main industrial sites of this area, where a medium sized coal power plant is located 5 Km NNE and a cogeneration plant burning coal and a pulp and paper plant are also placed 1 Km W.

Finally, Ni and V roses are plotted at Castro Urdiales (Fig. 7). It can be observed from this figure that Ni and V roses are similar, showing major peaks pointed into the direction of the main industrial areas where there are a petrochemical plant, a fuel-oil power station and some metallurgical factories. In addition, a lime and limestone production plant burning petroleum coke is also located 5 Km S, which can explain the peak pointed into the south.

Another peak toward SW direction is also found, but further investigation is needed in order to explain its origin, since no important sources are located in this direction.

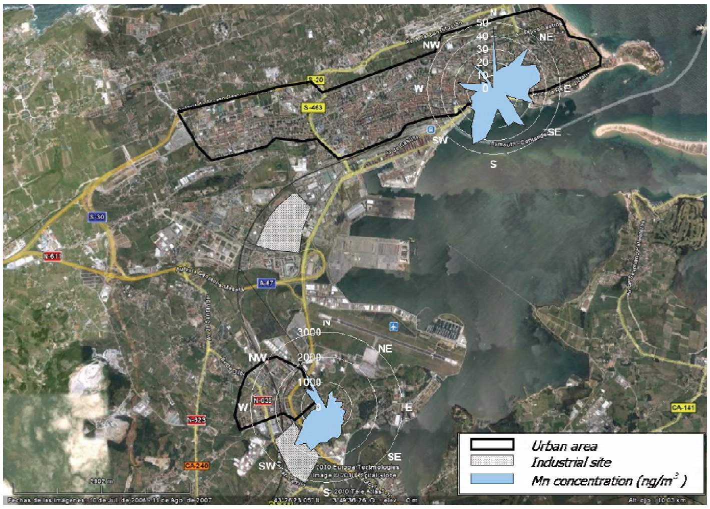
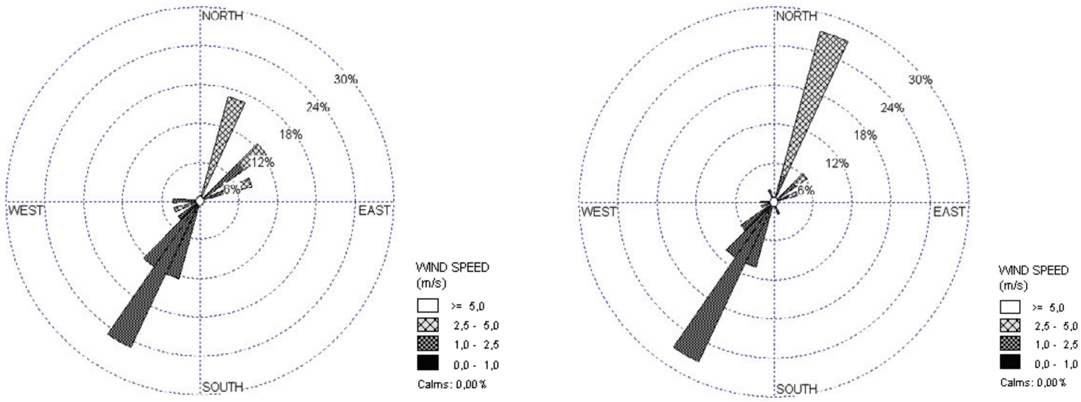


Figure 4. Mn roses at Santander bay



(a) (b)

Figure 5. Wind roses of the two days with the highest Mn concentration: a) 23/08/2008, 234.0 ngMn/m^3 b) 21/09/2008, 241.7 ngMn/m^3

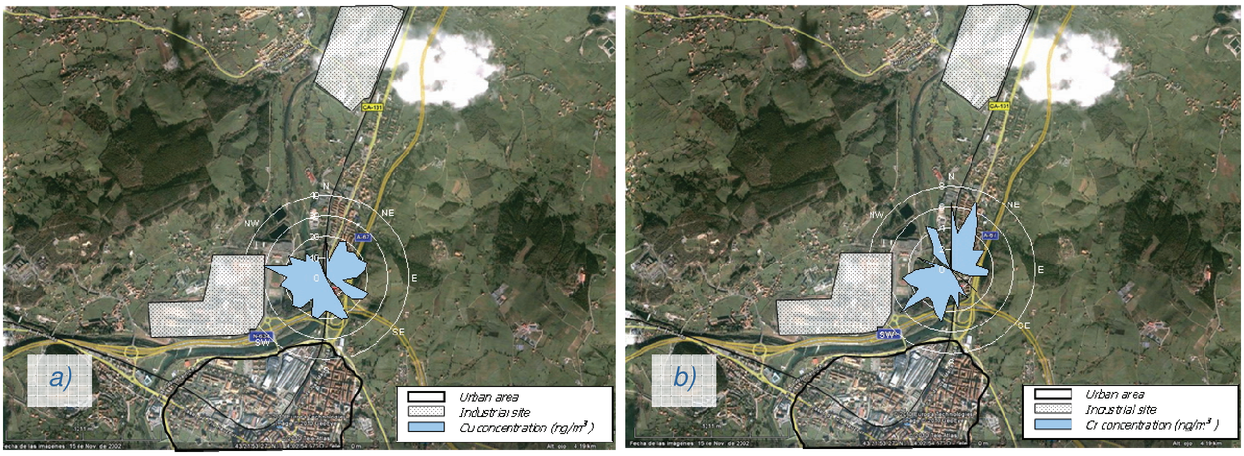


Figure 6. Pollution roses at TORR site: a) Cu b) Cr

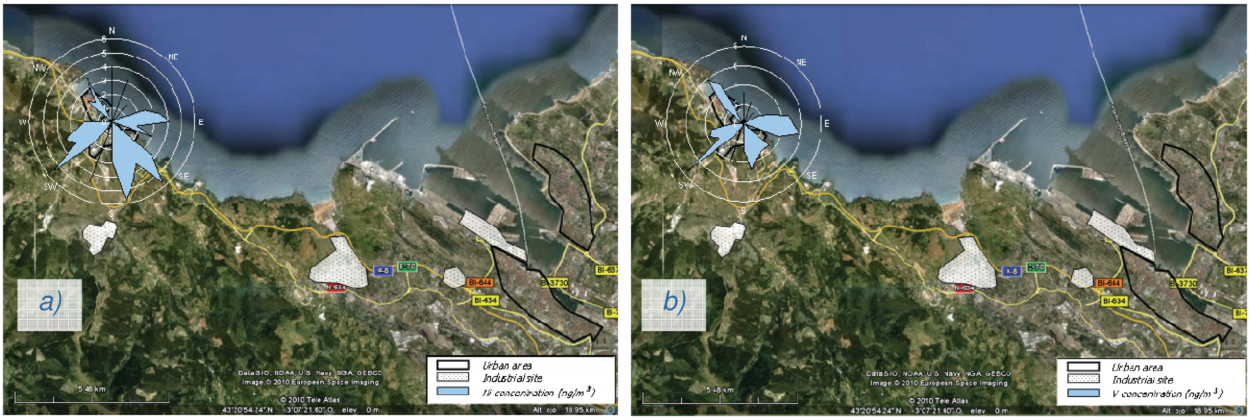


Figure 7. Pollution roses at CAST site: a) Ni b) V

4. Conclusions

The goal of this study was the evaluation of the impact of some industrial sources on trace metal levels in PM10 in the main urban areas of Cantabria Region (Northern Spain). Three urban areas were selected to carry out a chemical characterization of PM10 in 2008. In particular, we focused our attention on the emission sources using meteorological variables by means of pollution roses, because they can give us useful information on the trace elements distribution and, consequently, on their source profiles.

Among the studied trace metals, the EC regulated heavy metals (Pb, Cd, As, Ni) did not exceed the limit and target values set by the European Air Quality directives in the investigated period. The identification of the main tracers of each sampling site was performed by a ternary diagram and pollution roses of these tracers were then calculated and plotted onto satellite maps, leading to the following conclusions:

- Mn was identified as the main tracer at Santander: Mn roses at Santander bay are oriented toward the main industrial sites located SW of the Santander urban area.
- Cu and Cr were the main tracers at Torrelavega: Cu rose indicates that this metal is homogeneously distributed; therefore, it is assumed that traffic is the main source of Cu. While, Cr rose shows that the highest peaks are found when wind blows from SW and NE, where the main industrial sites are found.
- Ni and V were the main tracers at Castro Urdiales: the shape of both heavy metals roses is similar, thus

indicating that the same sources are contributing to the air levels of Ni and V at the studied site. The highest peaks pointed into the main industrial activities in this area.

Acknowledgements

The authors would like to thank the financial support of CTM 2006-00317 project (MEC) and the Government of Cantabria ("Actions for improving the air quality and its diagnosis in Cantabria") for their funding. We would like to express our gratitude to the Regional Environmental Ministry of Cantabria Government who kindly provided the dataset from ALM sampling point.

References

[1] C.A. Pope III and D.W. Dockery, J. Air Waste Manag. Assoc. 56 (2006) 709.
[2] T. Moreno, X. Querol, A. Alastuey, M. Viana, P. Salvador, A. Sánchez de la Campa, B. Artiñano, J. de la Rosa, W. Gibbons, Atmos. Environ. 40 (2006) 6791.
[3] M. Viana, X. Querol, A. Alastuey, F. Ballester, S. Llop, A. Esplugues, R. Fernández-Patier, S. García dos Santos, M.D. Herce, Atmos. Environ. 42 (2008) 1552.
[4] M. Viana, T.A.J. Kuhlbusch, X. Querol, A. Alastuey, R.M. Harrison, P.K. Hopke, W. Winiwarter, M. Vallius, S. Szidat, A.S.H. Prévôt, C. Hueglin, H. Bloemen, P. Wahlin, R. Vecchi, A.I. Miranda, A. Kasper-Giebl, W. Maenhaut, R. Hitzenberger, J. Aerosol Sci. 39 (2008) 827.
[5] D. Gladtke, W. Volkhausen, B. Bach, Atmos. Environ. 43 (2009) 4655.
[6] B. Bessagnet, A. Hodzic, R. Vautard, M. Beekmann, S. Cheinet, C. Honoré, C. Liousse, L. Rouil, Atmos. Environ. 38 (2004) 2803.
[7] S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, M.A. Trancoso, Sci. of the Total Environ. 368 (2006) 663.
[8] G. Cosemans and J. Kretzschmar, 9th Conf. On Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes, 2004.
[9] P. Lenschow, H.-J. Abraham, K. Kutzner, M. Lutz, J.-D. Preuß, W. Reichenbächer, Atmos. Environ. 35 Supplement No. 1 (2001) S23.
[10] M. Rigby, R. Timmis, R. Toumi, Atmos Environ. 40 (2006) 5112.
[11] M.C. Somerville, S. Mukerjee, D.L. Fox, R.K. Stevens, Atmos. Environ. 28 (1994) 3483.
[12] R.C. Henry, Y.-S. Chang, C.H. Spielgelman, Atmos. Environ. 42 (2002) 3964.
[13] R. Fernández-Camacho, J. de la Rosa, A.M. Sánchez de la Campa, Y. González-Castanedo, A. Alastuey, X. Querol, S. Rodríguez, Atmos. Res. 96 (2010) 590.
[14] M. Ragosta, R. Caggiano, M. D'Emilio, M. Macchiato, Atmos. Environ. 36 (2002) 3071.
[15] C. Mensink and G. Cosemans, 11th Int. Conf. On Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes, 2007.
[16] D.C. Snyder, J.J. Schauer, D.S. Gross, J.R. Turner, Atmos. Environ. 43 (2009) 4033.
[17] G. Cosemans, J. Kretzschmar, C. Mensink, Atmos. Environ. 42 (2008) 6982.
[18] G. Cosemans and J. Kretzschmar, 8th Conf. On Harmonisation within Atmospheric Dispersion Modelling fot Regulatory Purposes, 2002.
[19] A. Arruti, I. Fernández-Olmo, A. Irabien, J. Environ. Monit. 12 (2010) 1451.
[20] P.K.K. Louie, J.C. Chow, L.-W.A. Chen, J.G. Watson, G. Leung, D.W.M. Sin, Sci. Total. Environ. 338 (2005) 267.
[21] D. Howel, Chemosphere 67 (2007) 1300.
[22] J.P. Putaud, R. Van Dingenen, A. Alastuey, H. Bauer, W. Birmili, J. Cyrys, H. Flentje, S. Fuzzi, R. Gehrig, H.C. Hansson, R.M. Harrison, H. Herrmann, R. Hitzenberger, C. Hüglin, A.M. Jones, A. Kasper-Giebl, G. Kiss, A. Kousa, T.A.J. Kuhlbusch, G. Löschau, W Maenhaut, A. Molnar, T. Moreno, J. Pekkanen, C. Perrino, M. Pitz, H. Puxbaum, X. Querol, S. Rodriguez, I. Salma, J. Schwarz, J. Smolik, J. Schneider, G. Spindler, H. ten Brink, J. Tursic, M. Viana, A. Wiedensohler, F. Raes, Atmos. Environ. 44 (2010).1308.
[23] X. Querol, M. Viana, A. Alastuey, F. Amato, T. Moreno, S. Castillo, J. Pey, J. de la Rosa, A. Sánchez de la Campa, B. Artiñano, P. Salvador, S. García Dos Santos, R. Fernández-Patier, S. Moreno-Grau, L. Negral, M.C. Minguillón, E. Mofort, J.I. Gil, A. Inza, L.A. Ortega, J.M. Santamaría, J. Zabalza, Atmos. Environ.

41 (2007) 7219.
[24] X. Querol, A. Alastuey, M. Viana, S. Rodríguez, B. Artiñano, P. Salvador, S. García do Santos, R. Fernández Patier, C.R. Ruiz, J. de la Rosa, A. Sánchez de la Campa, M. Menéndez, J.I. Gil, J. Aero. Sci. 35 (2004) 1151.
[25] J.M. López, M.S. Callén, R. Murillo, T. García, M.V. Navarro, M.T. del Cruz, A.M. Mastral, Atmos. Res. 99 (2005) 58.
[26] C. Huelin, R. Gehrig, U. Baltensperger, M. Gysel, C. Monn, H. Vonmont, Atmos. Environ. 39 (2005) 637.
[27] N. Manalis, G. Grivas, V. Protonotarios, A. Moutsatsou, C. Samara, A. Chaloukou, Chemosphere 60 (2005) 557.
[28] A. Gaudry, M. Moskura, C. Mariet, S. Ayrault, F. Denayer, N. Bernard, Water Air Soil Pollut. 193 (2008) 91.
[29] G. Dongarrá, E. Manno, D. Varrica, M. Vultaggio, Atmos. Environ. 41 (2007) 7977.
[30] F. Cozzi, G. Adami, P. Barbieri, E. Reisenhofer, P. Apostoli, M. Bovenzi, Cent. Eur. J. Chem 8 (2010) 1014.
[31] M. Viana, X. Querol, A. Alastuey, J.I. Gil, M. Menéndez, Chemosphere 65 (2006) 2411.
[32] S.M. Boudissa, J. Lambert, C. Müller, G. Kennedy, L. Gareau, J. Zayed, Sci. Total Environ. 361 (2006) 67.
[33] M.L. Bosco, D. Varrica, G. Dongarrá, Environ. Research. 99 (2005) 18.
[34] T. Moreno, M. Pandolfi, X. Querol, J. Lavín, A. Alastuey, M. Viana, W. Gibbons. Environ. Sci. Pollut. Res. (2010) DOI 10.1007/s11356-010-0353-8.